Statistical and Thermal Physics: Homework 12

Due: 3 March 2020

1 Gibbs free energy and thermodynamic derivatives

a) Starting with $G = E - TS - PV$, express $\mathrm{d}G$ in terms of $\mathrm{d}T$ and $\mathrm{d}P$ and use the result to express S and V in terms of derivatives of G (remember to indicate variables in the parentheses subscripts).

b) Use the second derivative rule to show that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

2 Enthalpy and thermodynamic variables

a) Express $\mathrm{d}H$ in terms of $\mathrm{d}P, \mathrm{d}S$ and $\mathrm{d}N$ and use the result to express T, V, μ in terms of relevant derivatives of H (remember to indicate variables in the parenthesis subscript).

b) Show that

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$$

for any system.

3 Enthalpy for an ideal gas

The enthalpy of a system is

$$H = E + PV.$$

a) Show that

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V.$$

b) Use the previous result plus one of the Maxwell relations to show that for an ideal gas

$$\left(\frac{\partial H}{\partial P}\right)_T = 0.$$

4 Energy of a van der Waals gas

In general

$$\left(\frac{\partial E}{\partial T}\right)_V = c_V$$

and

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

a) Show that

$$\left(\frac{\partial c_V}{\partial V}\right)_T = T\frac{\partial^2 P}{\partial T^2}.$$

b) Starting with the equation of state for a van der Waals gas, show that

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{N^2}{V^2}a$$

and also that

$$\left(\frac{\partial c_V}{\partial V}\right)_T = 0.$$

c) Suppose that c_V is independent of temperature for a van der Waals gas. Use the previous results to determine an expression for the energy of the gas $E = E(V,T)$ in terms of c_V, N, V and a.

5 Heat capacities for water

Consider water at standard temperature and pressure (298 K and 1.01×10^5 Pa). The heat capacity at constant pressure per mole is $c_P = 73$ J/mol K. The (volume) thermal expansion coefficient is $207 \times 10^{-6}\,\mathrm{K}^{-1}$ and the isothermal compressibility is $3.57 \times 10^{-10}\,\mathrm{Pa}^{-1}$. Determine the heat capacity at constant volume, c_V, per mole under these conditions. Does it differ by much from c_P?